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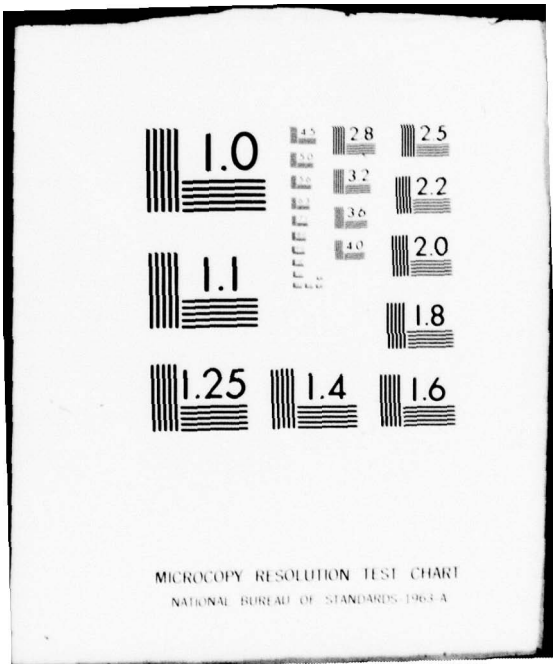
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LEVEL II

JP-4 FUEL STORAGE EMISSIONS

THOMAS B. K. STAUFFER
ENVIRONMENTAL SCIENCE DIVISION

DECEMBER 1978

FINAL REPORT SEPTEMBER 1977-DECEMBER 1978

CEEDO

CIVIL AND ENVIRONMENTAL
ENGINEERING DEVELOPMENT OFFICE
(AIR FORCE ENGINEERING AND SERVICES CENTER)
TYNDALL AIR FORCE BASE
FLORIDA 32403

PREFACE

This report documents work performed during the period September 1977 through December 1978 under Program Element 63723F, Project 2103, subtask 2C10. The work was done at Tyndall AFB with underground JP-4 storage tanks at Eglin AFB used for some of the studies. The author and principle investigator is Thomas B. Stauffer, research chemist.

The author wishes to thank the Fuels Management personnel at both Eglin AFB and Tyndall AFB for their help in fuel transfer operations during this study.

This report has been reviewed by the Information Office (OI) and is releaseable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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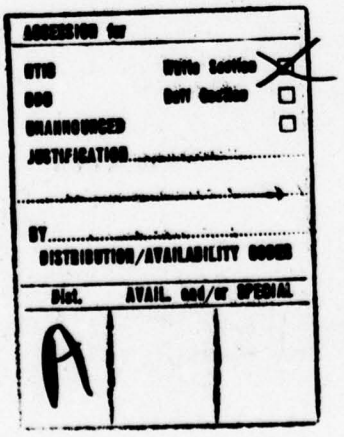

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

JP-4 vapors from underground fixed roof storage tanks were analyzed for hydrocarbon concentration by Gas Chromatography using a Flame Ionization Detector. Results are compared with predictions based on American Petroleum Institute correlations. Since Air Force tanks are normally refilled within 24 hours of emptying, only turnover times of 24 hours and less were considered. It was found that within 24 hours tank air reached only 75-85 percent of saturation for JP-4. At turnover times of 7.5 hours and less a marked layering of vapor

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concentration could be measured in the expelled air. Actual mass emissions are less than predicted by equations because of the rapid turnover and consequential reduction in vapor concentration. Data presented provide a basis for calculating a rough estimate for hydrocarbon mass emitted based on fuel storage temperature. Actual mass emissions measured during the study varied from 0.6 to 1.5 lb/1000 gal of JP-4 transferred while the fuel temperature ranged from 51°F to 79°F.

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SECTION I

INTRODUCTION

Evaporative hydrocarbons are receiving close scrutiny from various air quality control agencies such as the Environmental Protection Agency (EPA) and the South Coast Air Quality Management District (SCAQMD) of Southern California. Current standards require that underground fuel tanks of 40,000 gallons capacity or greater must be equipped with a vapor control device if the stored hydrocarbon fuel has a true vapor pressure (TVP) of 1.5 psia or above. This standard is suggested by the EPA as a minimum standard, but it is the responsibility of each state to determine its own air quality standards. Because each state may have a different standard, the Air Force may be compelled to abide by a variety of air quality standards depending on the location of a given base.

The Air Force currently has numerous 50,000 gallon tanks in its inventory that are used for the storage of JP-4, a hydrocarbon based fuel used in most Air Force aircraft. The TVP of a hydrocarbon fuel is a function of storage temperature, and at temperatures greater than approximately 70^{o}F JP-4 exceeds the 1.5 psia regulation. Fuel storage temperatures in the desert regions of California frequently exceed 70^{o}F during the summer months, several bases in southern California have been cited for non-compliance. SCAQMD air quality regulations require vapor recovery devices of 95 percent efficiency for the Los Angeles basin and 90 percent efficiency for the High Desert area (Reference 1).

Air Force officials felt that even though the vapor pressure standard was being exceeded, the actual mass, i.e., pounds of hydrocarbons emitted, was small. The object of this project was to measure the mass of hydrocarbons emitted during normal operation of underground JP-4 storage tanks. The data obtained can be used to calculate actual mass emissions which can then be used to model air base pollution loads and to answer air regulatory agencies questions concerning hydrocarbon emissions. The data may also be used at bases in areas where regulatory standards are based on mass emissions or as design criteria for vapor control devices.

SECTION II

EXPERIMENTAL METHODS

Infrared (IR) Spectroscopy and Gas Chromatography (GC) were examined as possible candidates for quantitating JP-4 vapors. Some preliminary work was done with JP-4 vapor using a Wilks Miran I IR to measure the C-H stretching frequency and quantitate vapor emissions. Since the absorbtivity of JP-4 was so high, a very short path length flow cell was necessary to continuously monitor the tank effluent. No small flow cell could be found that worked well and IR was abandoned in favor of GC using a flame ionization detector (FID).

An Analytical Instruments Division, Inc. (AID) Portable Gas Chromatograph equipped with FID was used for quantitating the JP-4 vapor concentration. This instrument was equipped with both a sample loop injection system and a septum injection system. There was also a columm bypass valve which passes samples from the injection port directly to the FID giving the total hydrocarbon concentration (THC) of the sample.

Two different methods were used to calibrate the GC - FID and quantitate the JP-4 vapors. One method used direct syringe injection of both vapor and standards and the second method used the sample loop injection system. Using the sample loop necessitated a dilution of the gas to work in the linear response range of the FID.

A 100 µl gas syringe was used to inject the sample and standards in the direct injection technique. Standards were prepared from methane and nitrogen in a 100-ml round bottom flask equipped with a Teflon® vacuum valve and a silicon rubber septum. A Wallace-Tiernan absolute pressure guage was used to monitor the required partial pressures of the gases. Flasks were prepared to encompass the range from 76 Torr to 380 Torr of methane with a total pressure of 760 TORR. This corresponds to 10 percent to 50 percent methane equivalent (ME). A calibration curve of peak height versus injections of varying percent methane equivalents is shown in Figure 1.

Samples of vapor from the JP-4 tanks were collected from the vent pipes by pulling air directly into the gas syringe and flushing several times before actual injection into the GC. Figure 2 shows a typical underground JP-4 storage tank system. The tanks are right cylinders placed on their sides approximately 12 ft in diameter by 60 ft long. A four-inch pipe is used as a vent and is located near one end of the tank extending about eight ft above ground level. The vent pipe is usually equipped with a vacuum/pressure relief valve set to open at approximately 3 inches of water pressure. During normal filling operations these valves opened seconds after the pumps started filling the tank.

The second sampling system used the sample loop within the GC and required a different mode of operation and calibration. The sample loop volume was approximately 0.7 ml, consequently introducing samples of JP-4

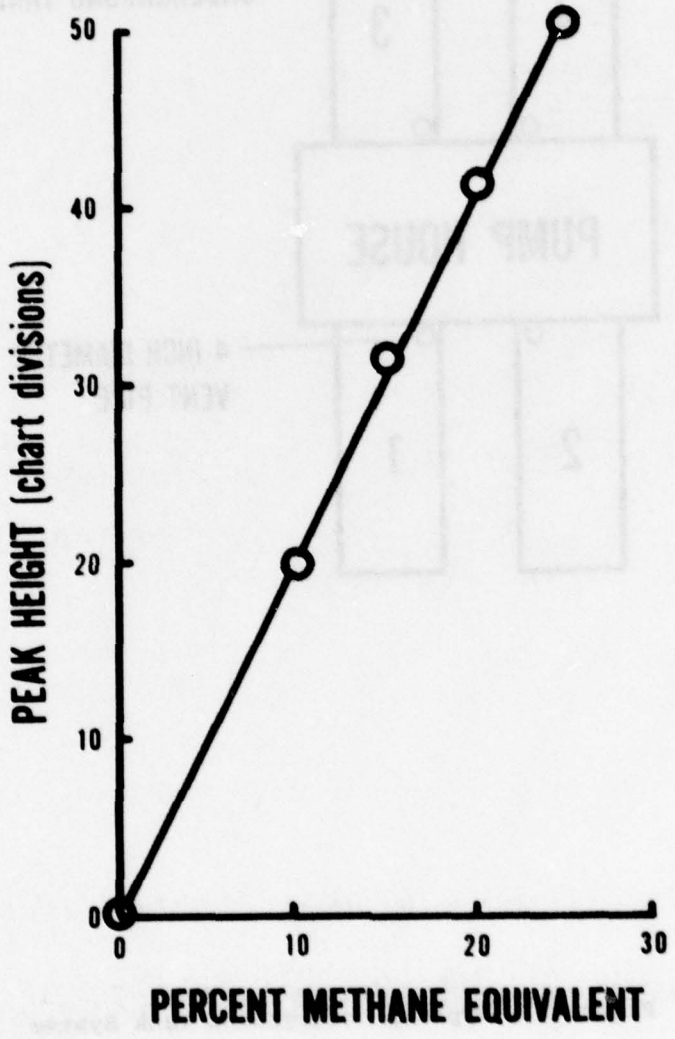

Figure 1. Calibration Curve for Syringe Injections

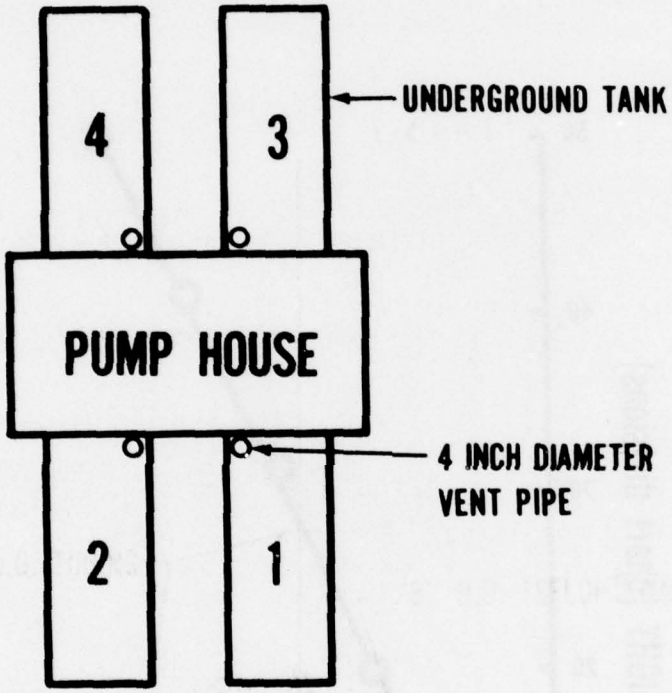

Figure 2. Typical Underground Tank System

vapor of this volume drove the FID out of its linear operating range. Since no different volume loops were available, the sample was diluted to bring the response of the FID into the linear range. Dilution was effected by means of a splitter as shown in Figure 3. The split ratio was varied by adjusting the needle valve and was measured with an inverted soap bubble flow meter.

Hydrocarbon standards for the loop system were prepared by using a gas proportioner which blends two gases to form a homogeneous mixture. Methane, propane, and butane were used to prepare mixtures from 10 percent to 50 percent ME. The mixtures were prepared by setting the rotameters on the proportioner to produce known flows of the hydrocarbon and air. Rotameters were calibrated with a soap flow meter for low flow rates (< 1 ℓ/min) and a wet test meter for high flow rates (> 1 ℓ/min. The percent methane equivalent was then calculated from the flow rate data for the mixtures produced. The blended mixtures were flowed into a tedlar bag and then the splitter was placed in the bag and used to fill the sample loop. The loop was filled by connecting a Thomas Industries, Inc air pump equipped with Teflon ® internal parts to the exit side of the sample loop on the GC. When the pump was started, gas samples were drawn through the splitter and into the 1/8 inch Teflon® tubing connecting the splitter to the sample loop. Turning the sampling valve then introduced the gas to the FID. Again a curve of recorder response or peak height versus percent ME was plotted to quantitate the concentration of JP-4 vapors.

Samples for the sample loop system were obtained by inserting the side arm of the splitter into a small hole cut into a 10-foot section of four-inch galvanized tin stove pipe placed in the JP-4 tank vent pipe. Again the splitter was connected to the GC by Teflon® tubing and the air pump used for drawing samples through the system. As an additional safety precaution, a flash arrestor was placed in the tubing line between the splitter and the GC to insure that the flame from the detector could in no way ignite the JP-4 vapor in the tank.

A F. W. Dwyer Mfg model 160-18 pitot tube was connected to a Magnehelic guage and inserted into the stove pipe to measure changes in pressure caused by the flowing JP-4 vapors. Pressure readings were monitored continuously during fill operations, so that the total volume of gas expelled could be calculated. The stove pipe provided the extra length required to prevent errors in measuring the gas velocity.

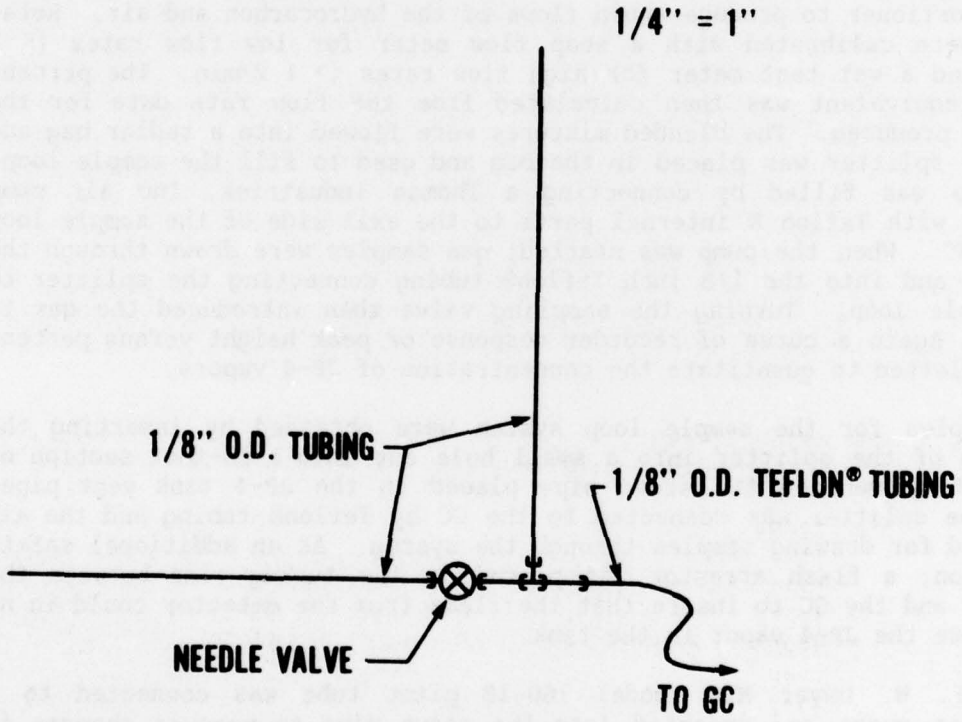

Figure 3. Sample Splitter

SECTION III

RESULTS

JP-4 vapors expelled from 25,000 gal tanks at Tyndall AFB were measured on three separate occasions. The first run was conducted on Oct 3, 1977 when the fuel temperature was 80°F and air temperature was 75°F. Sixteen thousand one hundred eight gallons were transferred and the average concentration of JP-4 vapors was 23.6 percent ME. The second run was conducted on Oct 19, 1977 with a fuel temperature of 74°F and air temperature of 73°F. Nineteen thousand seven hundred eighteen gallons of fuel were transferred in 32.5 minutes. Table 1 gives the concentration in Methane Equivalents measured during the fuel transfer operation. The overall average for the entire operation was 23.9 percent ME. The third and final run at Tyndall was conducted on Dec 15, 1977 when the fuel temperature was 69°F and air temperature was 63°F. Eighteen thousand three hundred eighty four gallons of fuel were transferred and the average vapor concentration was 26.4 percent ME. Table 2 gives the concentration of the vapors measured during the run. The tank next to the study tank was also being filled and was grab sampled periodically, and the average for this tank was 26.9 percent ME. A typical calibration curve for these runs is shown in Figure 1. For all three runs the tanks were drawn down to a low level of JP-4 and allowed to sit "empty" for approximately 24 hours before refilling.

A second series of experiments were conducted at Eglin AFB on February 1, 1978 using 50,000 gallon underground tanks. The object of this study was to evaluate the effect of turnover rate on vapor saturation. Figure 2 shows the tank layout. Tank #2 was emptied on January 31, 1978 at 1215 and Tank #1 was emptied on February 1, 1978 at 0650. JP-4 vapor concentrations were measured as fuel was transferred between tanks #1 and #3 and tanks #2 and #4. Weather conditions were unfavorable with rain falling and air temperature 44°F. The fuel temperature was 51°F. Fuel was transferred from tank #4 to tank #2 while the JP-4 vapor concentration was monitored. The average concentration was 14.3 percent ME for the 24 hour empty period as shown in Figure 4. At 1415 fuel was transferred from tank #3 to tank #1 which had been emptied that morning at 0650. Figure 5 shows the percent methane equivalent versus time for the 7.5 hour empty period, resulting in an average vapor concentration of approximately 15 percent methane equivalent. Tank #2 was then pumped into tank #4 after it had sat empty from about 1415 to 1530 or about 1.25 hours. Figure 6 shows the possible layering of vapor concentration observed during this rapid turnover/refill sequence. This run was terminated before the tank was completely filled for operational reasons.

On May 25, 1978 two more tanks were analyzed at Eglin AFB, Florida. The object of this study was to critically evaluate vapor layering at short turnover intervals. The fuel temperature was 70°F and the air temperature was 86°F. Tank #1 was emptied at 0845 and was refilled from tank #3 starting at 1115. Figure 7 shows the gradual increase in vapor

TABLE 1. HYDROCARBON RESULTS FROM TYNDALL AFB OCTOBER 19, 1977

Time (Local)	Concentration (Percent Methane Equivalent)
1323*	0
1326*	0
1328	23.7
1330	24.5
1332	24.7
1334	25.7
1336	24.2
1338	25.5
1340	25.5
1342	23.2
1344	23.2
1346	23.2
1348	22.5
1350	22.2
1352	22.7
1354	24.0
1355*	0
1358*	0

*Pressure/vacuum valve closed

TABLE 2. HYDROCARBON RESULTS FROM TYNDALL AFB DECEMBER 15, 1977

Time (Local)	Concentration (Percent Methane Equivalent)
1320*	0
1321	25.0
1322	26.3
1323	26.3
1324	25.7
1325	28.0
1328	24.0
1330	26.3
1332	25.9
1333	26.3
1335	32.0
1337	32.6
1338	29.4
1339	30.4
1340	31.2
1342	30.0
1343	28.2
1346	27.6
1347	29.4
1348	25.0
1349	23.4
1351	23.4
1353	23.4
1355	23.4
1357	24.7
1358	24.7
1359	23.4
1403	22.2
1405	23.4
1407	23.4
1408*	0

*Pressure/vacuum valve closed.

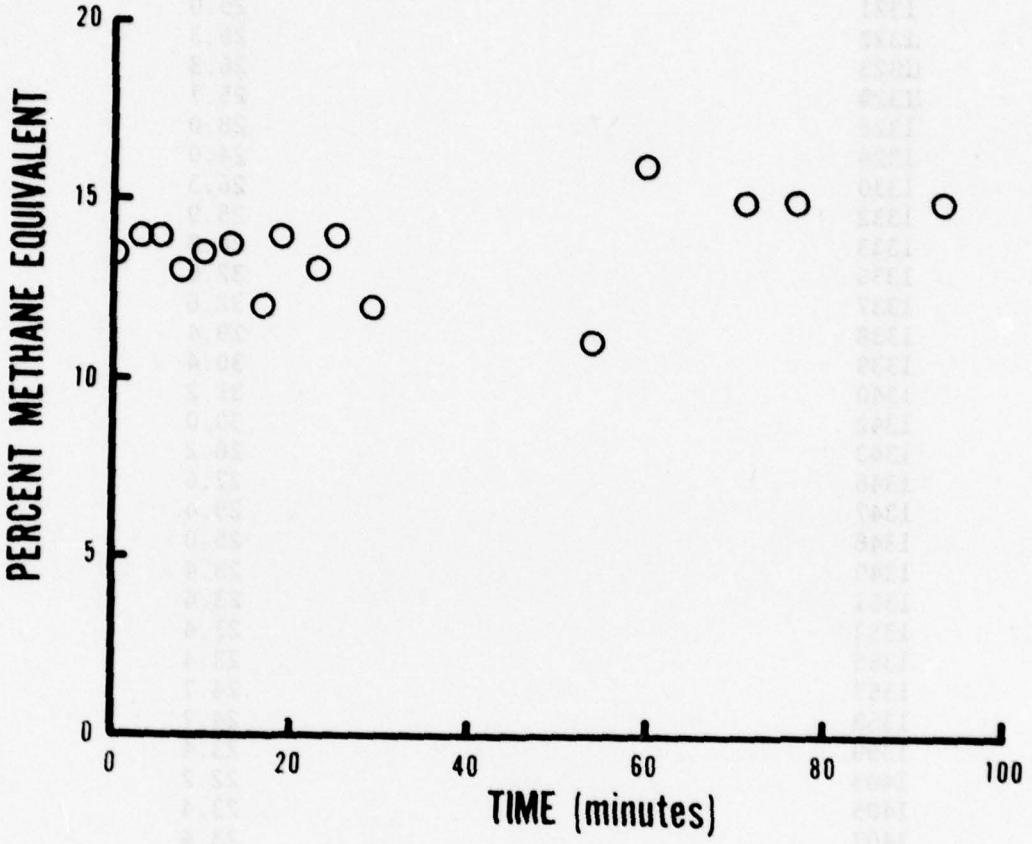

Figure 4. Vapor Concentration During Fuel Transfer, February 1, 1978

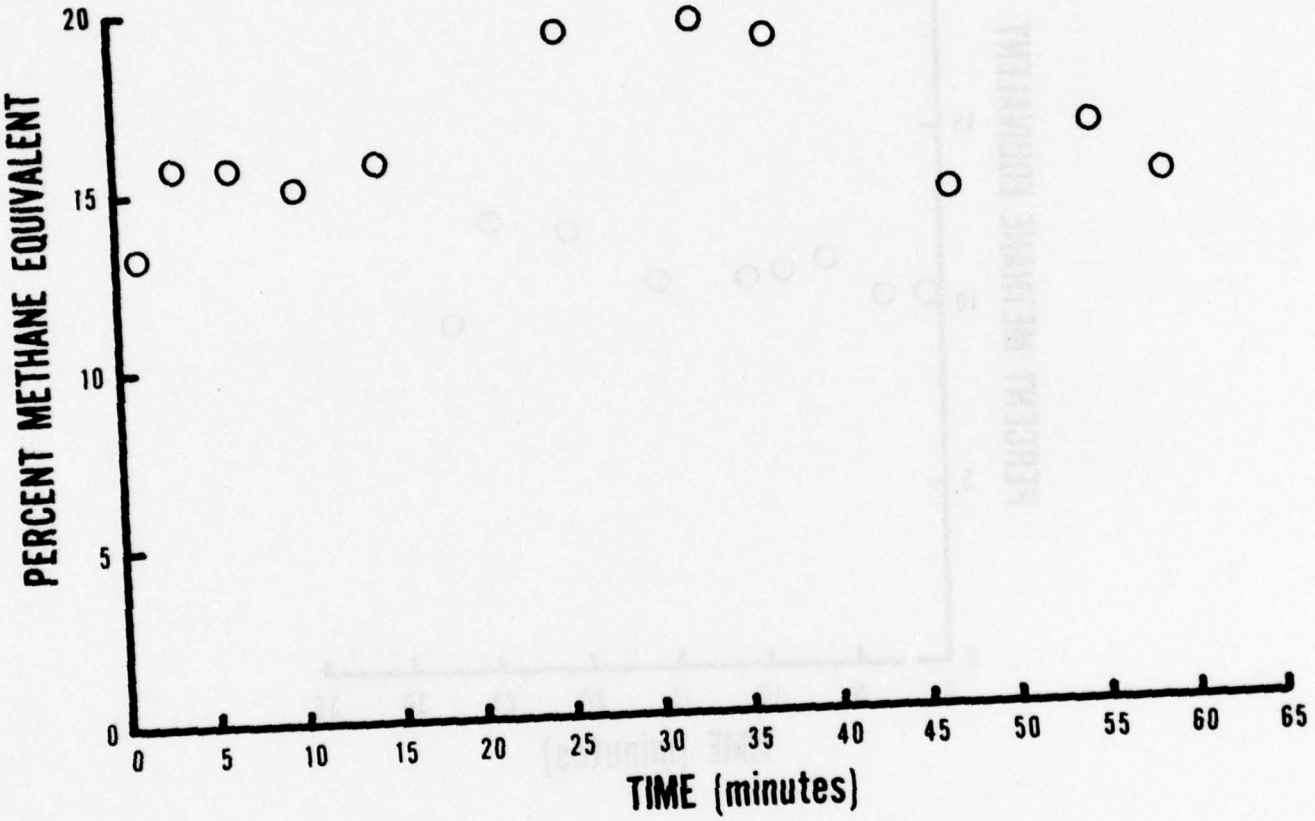

Figure 5. Vapor Concentration for 7.5 Hour Turnover, February 1, 1978

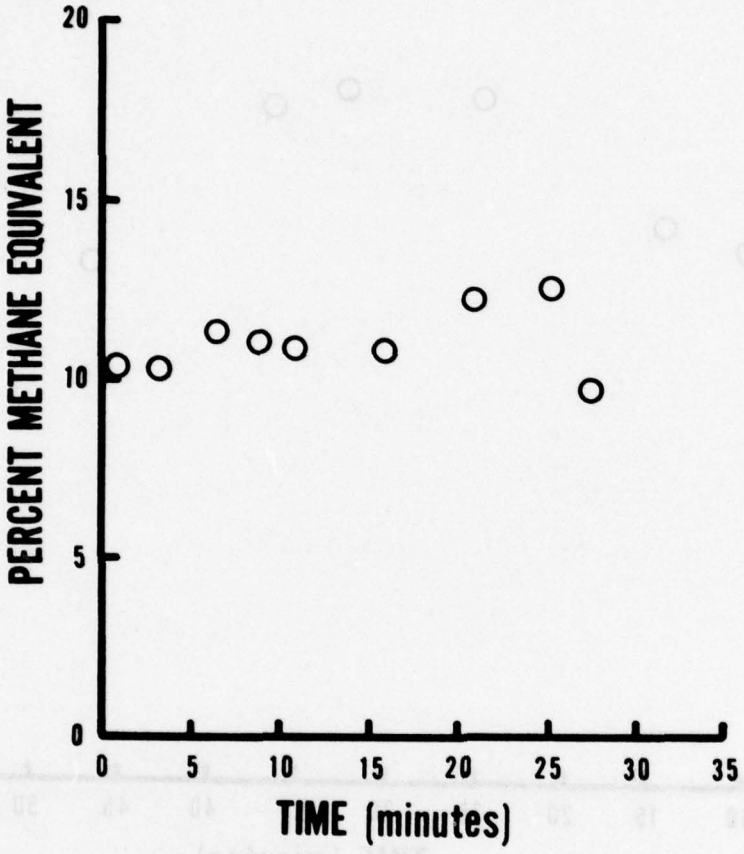

Figure 6. Vapor Concentration for 1.25 Hour Turnover, February 1, 1978

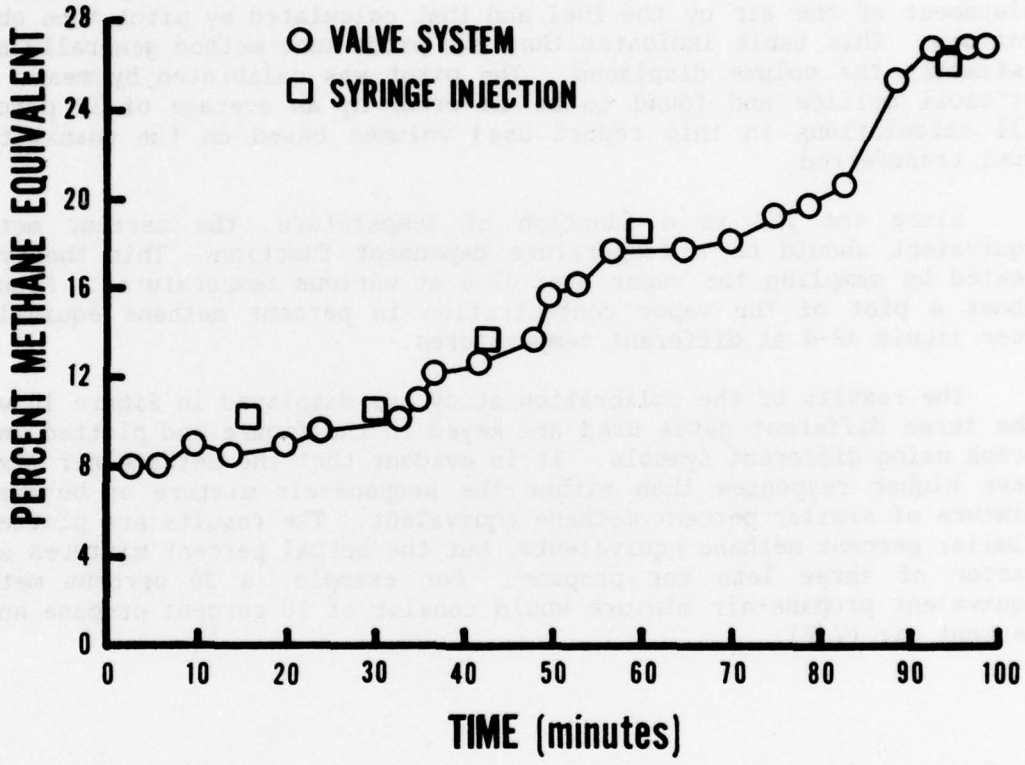

Figure 7. Vapor Concentration for 2.5 Hour Turnover, May 25, 1978

concentration during this run. The vapor concentration ranged from 7.6 to 26.8 percent ME. Immediately following the transfer from tank #3 to tank #1 the fuel in tank #1 was pumped back into tank #3 and the vapor concentration measured. Results from this operation are shown in Figure 8. Data from 78 minutes to 110 minutes were extrapolated because a rain shower interrupted the study by clogging the splitter. The 110 minute point was obtained by syringe injection of the expelled vapor. The range of concentrations observed was from 5.2 percent to 25.6 percent ME.

Table 3 gives a comparison of the volume calculated by simple displacement of the air by the fuel and that calculated by pitot tube observations. This table indicates that the pitot tube method generally overestimates the volume displaced. The pitot was calibrated by means of a critical orifice and found to be in error by an average of 12 percent. All calculations in this report used volumes based on the quanitity of fuel transferred.

Since the TVP is a function of temperature, the percent methane equivalent should be a temperature dependent function. This theory was tested by sampling the vapor over JP-4 at various temperatures. Figure 9 shows a plot of the vapor concentration in percent methane equivalents over liquid JP-4 at different temperatures.

The results of the calibration study are displayed in Figure 10 where the three different gases used are keyed in the figure and plotted on the graph using different symbols. It is evident that the Methane-air mixture gave higher responses than either the propane-air mixture or butane-air mixture of similar percent methane equivalent. The results are plotted as similar percent methane equivalents, but the actual percent mixtures are a factor of three less for propane. For example, a 30 percent methane equivalent propane-air mixture would consist of 10 percent propane and 90 percent air (V/V).

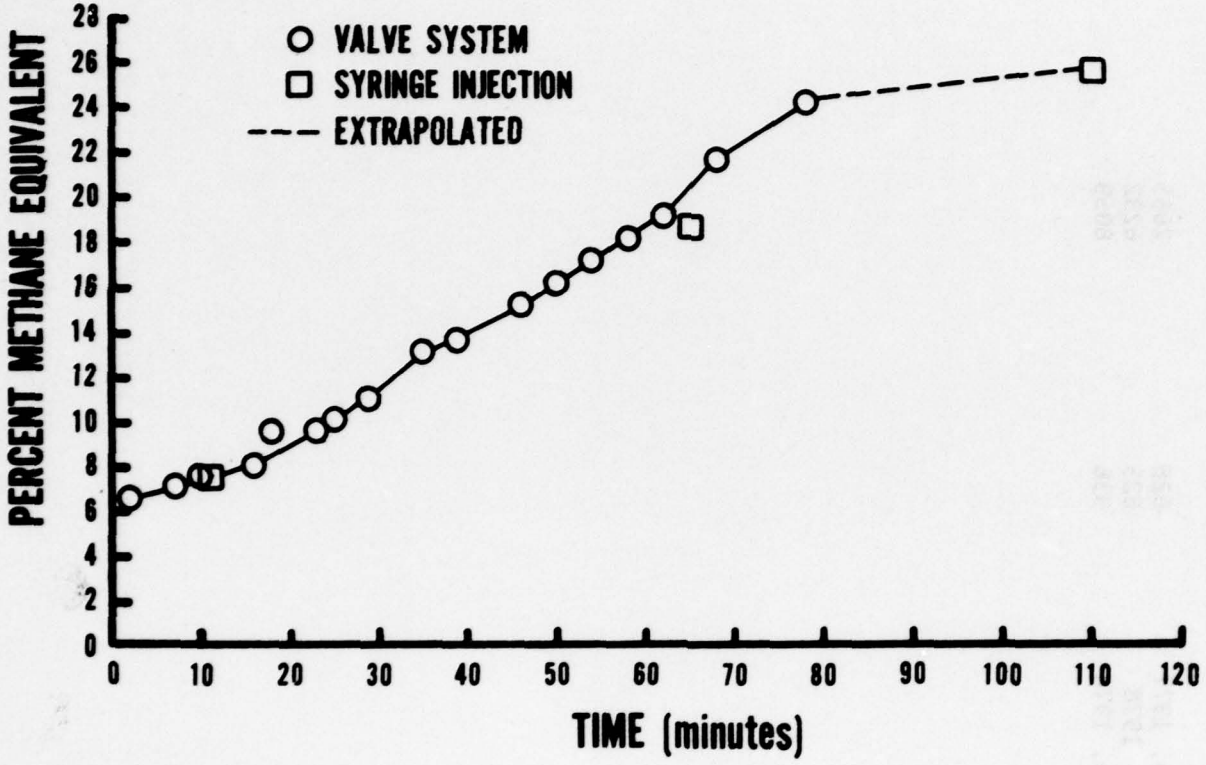

Figure 8. Vapor Concentration 0 Hour Turnover, May 25, 1978

TABLE 3. COMPARISON OF PITOT TUBE VOLUMES AND DISPLACED VOLUMES

Run Date	Average Velocity (ft/min)	Pitot Volume (ft^3)	Displaced Volume (ft^3)
Dec 15, 1977	628	2665	2458
Feb 1, 1978	825	6232	5795
May 25, 1978	936	8059	6149

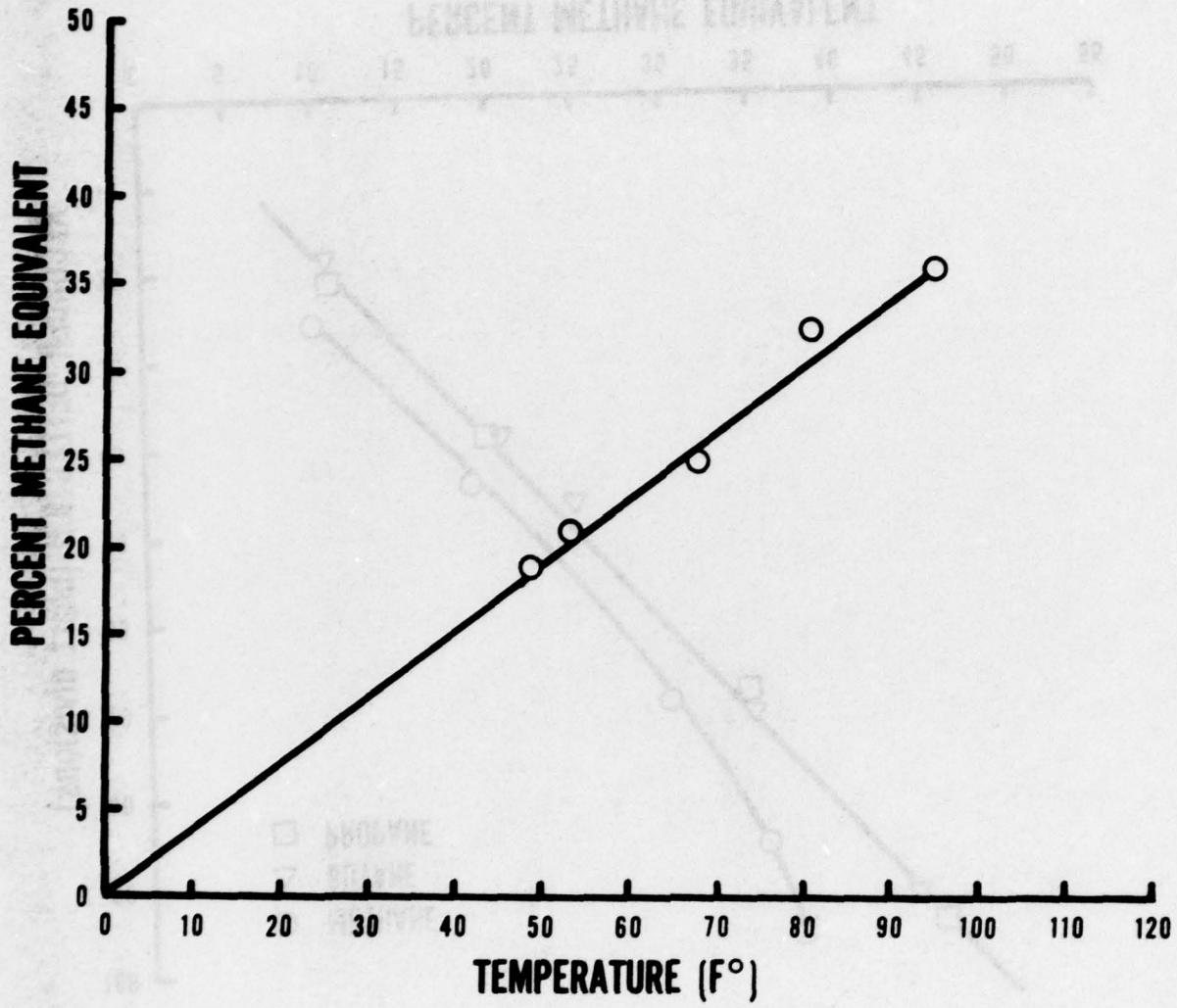

Figure 9. Concentration of Vapor Over Liquid JP-4 Versus Temperature

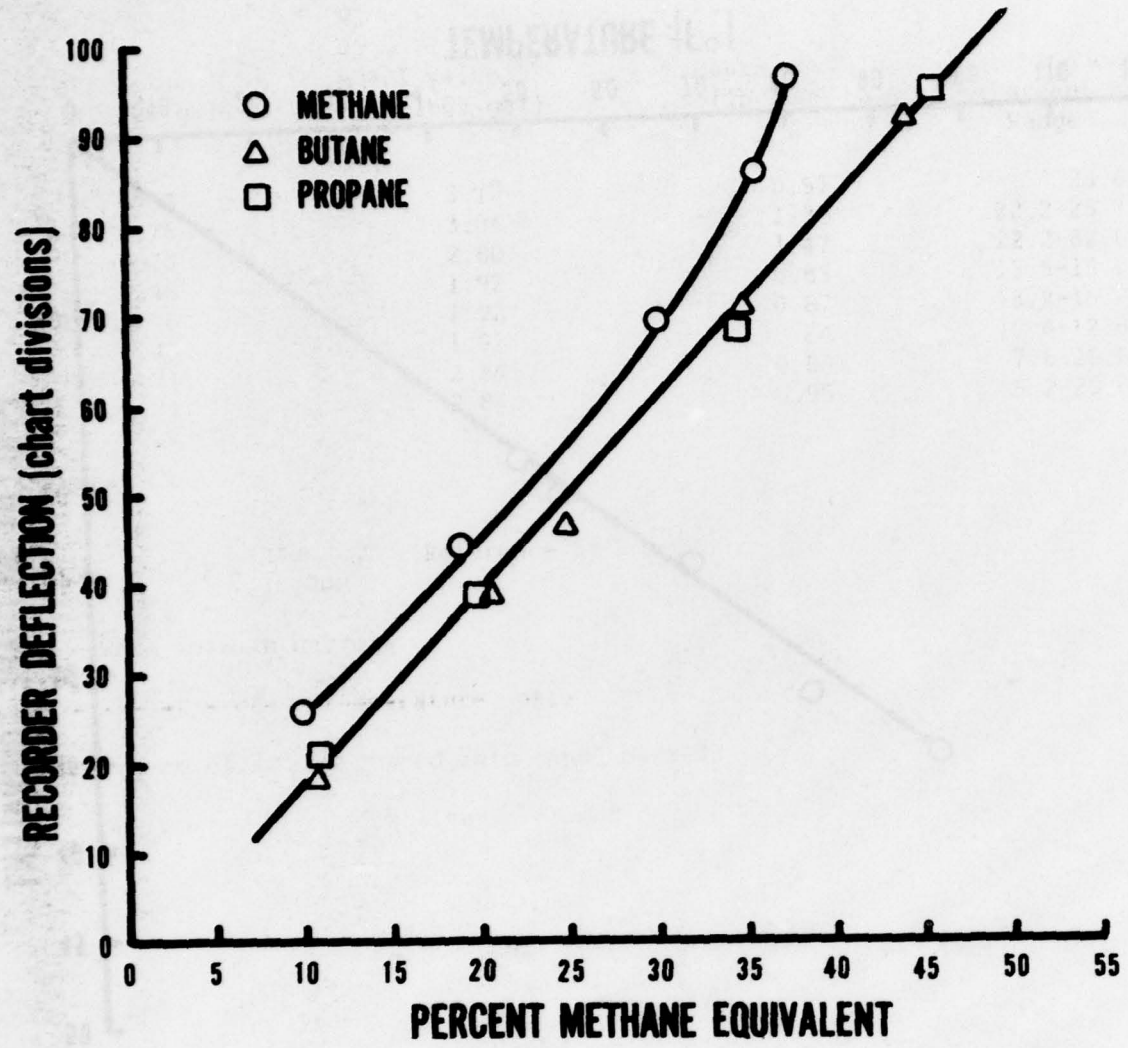

Figure 10. Calibration Curves for Methane, Propane, and Butane

SECTION IV

DISCUSSION

Only working losses were considered in this report because breathing losses are of little consequence in underground fixed roof tanks since fuel temperatures fluctuate slightly. Working losses are produced by filling and emptying tanks, because air inhaled during emptying is expelled when the tank is refilled. Since tanks are never truly emptied, i.e., there is always a liquid layer of fuel in the bottom of the tank, the inhaled air becomes laden with JP-4 vapor. When the tank is cycled the JP-4 vapor is displaced into the atmosphere and becomes an air pollution problem.

The American Petroleum Institute (API) Bulletin 2513 (Reference 2) discusses methods for calculating working losses from underground fixed roof tanks. The original intent of this document was to point up the economic significance of controlling vapor losses. When air pollution agencies started instituting air quality standards, the API formulas were applied to quantitate emissions. Since then, the validity of the API formulas has received considerable scrutiny. Engineering-Science, Inc prepared a report (Reference 3) for Western Oil and Gas Association on hydrocarbon emissions from fixed-roof tanks, in which they determined that total emissions were only about 55 percent of that calculated by API correlations. Both the API and Engineering-Science, Inc work have been primarily with gasoline type fuels with little or no attention given to the petroleum fraction that JP-4 resembles.

Only one other study could be found where JP-4 vapors were analyzed (Reference 4). This study sampled two tanks; one had been empty for seven days and the other had been empty for less than 24 hours. Percent methane equivalents for the seven-day tank ranged from 45 percent to 57 percent and for the 24-hour tank from 35 percent to 50 percent. Both tanks were also cleaned prior to testing which is not typical Air Force operating procedure. No temperature data were reported.

Table 4 summarizes the average mass emission results obtained in this study. Comparing the values obtained with those predicted by the API equations shows that the API would predict higher emissions if the turnover factor was 1.0 and would underestimate emissions if the turnover factor was 0.25. The API defines turnover as the annual through-put in gallons divided by the tank capacity in gallons (Reference 5). Use of this definition would require that 1.0 be used as the turnover factor on all tanks studied in this report. The intent of the turnover factor was to account for differences in vapor concentration caused by varying contact times of inhaled air with the hydrocarbon liquid in the tank. In Reference 5 a figure is given to enable the user to pick the appropriate turnover factor. At 36 or more turnovers per year, the factor is 0.25.

The actual operation of the tank is the critical aspect of the problem because this determines the length of time that the inhaled air is

TABLE 4. COMPARISON OF API CALCULATED EMISSION AND MEASURED EMISSIONS

Date	API Value (1) (lb/1000 gal)	API Value (2) (lb/1000 gal)	Measured Value (lb/1000 gal)	Concentration (Percent Methane Equivalent) Range	Average
Oct 3, 1977	0.78	3.12	0.91	23.6	23.6
Oct 19, 1977	0.76	3.04	1.32	22.2-25.7	23.9
Dec 15, 1977	0.70	2.80	1.47	22.2-32.6	26.4
Feb 1, 1978	0.48	1.92	0.83	13.5-15.0	14.3
Feb 1, 1978	0.48	1.92	0.87	13.2-16.2	15.1
Feb 1, 1978	0.48	1.92	0.64	10.4-12.6	11.1
May 25, 1978	0.71	2.84	0.85	7.6-26.8	15.5
May 25, 1978	0.71	2.84	0.95	5.2-25.6	17.4

(1) Calculated from $F = \frac{3PV}{10,000} KT$ (Reference 5)

where F = Work loss in barrels

P = TVP at storage temperature, psia

V = Volume of liquid pumped into tank, barrels

KT = Turnover factor, for 1 turnover per day KT = 0.25

(2) KT = 1.0

in contact with liquid fuel. The longer the air lays in contact with the fuel the more hydrocarbon evaporates into the air. If the air is not completely mixed or saturated, layers of increasing hydrocarbon content will form in the tank. At turnover times of 7.5 hours to 24 hours, no significant layering could be detected. Turnover times of 2.5 hours and 0 hours showed considerable layering as shown in Figures 7 and 8. It is apparent that if the tanks are immediately refilled after emptying, the mass of hydrocarbon emitted on refilling is reduced. The amount of reduction depends on how the tank was emptied. If it was drawn down from full to empty, and immediately refilled, the emissions would be reduced more than if the tank was emptied by stages and then immediately refilled when emptied.

To obtain an idea of how fuel temperature influences emissions, the vapor over solutions of JP-4 was analyzed for percent methane equivalent as a function of temperature as shown in Figure 9. As the fuel temperature increases so does the TVP and concentration of JP-4 in the vapor. Table 5 compares the concentration of JP-4 in the vapor phase from storage tanks with the laboratory studies at similar temperatures. Only tanks that were empty for 24 hours before refilling are considered here. The table shows that the JP-4 in the tanks was not saturated at the fuel storage temperature. Only in one case did the vapor approach saturation and this occurred at 69°F. In the other instances the vapor was 75-85 percent of the measured saturation value. It appears that in 24 hours the inhaled air only becomes 75-85 percent saturated. The 24 hour period was picked as a maximum empty period because tanks are usually drawn down during the normal duty day and refilled on the second or third shift.

Figure 9 may be used to obtain an estimate of the mass emissions from underground tanks for various temperatures. The mass calculated by this method would be a worst case as discussed above.

The results displayed in Figure 10 show there is a slight difference between methane, and propane and butane equivalents. The reason for this discrepancy is unresolved. Propane and butane curves were obtained because results from other studies are reported as propane equivalents and it was necessary to insure there were no major differences among the calibration gases. The difference is less than 3 percent methane equivalent in the region of the curve utilized in this study and is therefore not considered a serious source of error.

TABLE 5. COMPARISON OF TANK VAPOR CONCENTRATION AND SATURATED VAPOR CONCENTRATION

Fuel Temperature (F^{o})	Air (F^{o})	Tank Concentration (Percent Methane Equivalent)	Saturated Vapor (Percent Methane Equivalent)
80	75	23.6	30.2
74	73	23.9	28.0
69	63	26.4	26.2
51	44	14.3	19.2

SECTION V

SUMMARY

Results show that JP-4 emissions from underground storage tanks are dependent on the working schedule of the tanks and fuel storage temperature. API correlations overestimate the mass emitted during fill operations if a KT factor of 1.0 is used. The KT factor as defined by the API is probably not applicable to Air Force operations since tanks may be worked only occasionally but refilled soon after emptying.

Currently most regulatory agencies use TVP as the only criteria for requiring installation of vapor recovery devices. However, these studies show that working schedule affects the mass emission as well as TVP. Since the concentration of the vapors measured in this study generally failed to reach saturation, JP-4 emissions are less than would be predicted if only the TVP is considered.

It appears that in a 24 hour cycle the inhaled air does not reach complete saturation. Turnover periods of 2.5 hours and less show strong vapor layering within the tank. This layering fades after about 8 hours and at 24 hours no distinct increasing vapor concentration trend could be detected.

Mass emissions varied from 1.47 lbs/1000 gal to 0.64 /lb 1,000 gal depending on tank fill schedule and fuel storage temperature. Results given in this report permit a worst case mass emission calculation based on fuel temperature.

REFERENCES

1. South Coast Air Quality Management District of California Rule 463 - Storage of Organic Liquids.

2. "Evaporation Loss in the Petroleum Industry - Causes and Control", American Petroleum Institute Bulletin 2513, February 1959.

3. "Hydrocarbon Emissions from Fixed-Roof Petroleum Tanks" Report, Engineering-Science, Inc, July 1977.

4. "Analysis of Fuel Storage Tank Emissions", F. N. Hodgson, Monsanto Research Corp, Report 76-15, September 13, 1976.

5. "Evaporation Loss from Fixed-Roof Tanks", American Petroleum Institute Bulletin 2518, June 1962.

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